Cavity Ring-Down Laser Spectroscopy of Carbon-Chain Molecules

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spectra of the origin and a large set of vibronic bands coincided with some DIBs within a ±2 Å limit [57]. The hypothesis that C_7^- is a carrier of DIBs had, however, to be withdrawn on the basis of subsequent high-quality astronomical data [58]. Spectroscopic investigations provided evidence that bare carbon chains such as C_5, C_6, ... C_{15}, as well as their cations and anions or their derivatives containing H or N are not responsible for the stronger DIBs features [59]. The cases for other carbon-based molecules such as l-C_3H_2, $HC_{2n}H^+$, C_{60}^+ and carbon rings of the size up to a hundred of atoms have been discussed in Refs. [59–61].

1.2 Thesis outline and summary

A variety of laser-based spectroscopic techniques have been used to record optical transitions of carbon-based molecules [62]. The general methodology for recording high-resolution gas-phase spectra of such species is to first record an absorption spectrum via matrix isolation spectroscopy. With the matrix data available, the gas-phase spectra of the neutrals and ionic radicals can be measured by a number of methods, such as cavity ring-down spectroscopy (CRD), resonant two-color two-photon ionization (R2C2PI), laser-induced fluorescence (LIF), trapped-ion photo fragmentation, and photo-detachment spectroscopy. The gas phase data provided by these techniques, specifically the methods based on recording direct absorption spectra, can be compared with observational data, for instance the DIBs profiles. As a second goal of high-resolution spectroscopic studies, geometrical and electronic structures of carbon-based molecules can be characterized.

In this thesis, laser spectroscopy of (hydro)-carbon-chain radicals of astrophysical interest is reported. Sensitive pulsed cavity ring-down techniques, combined with molecule formation in an expanding plasma, enable to record high-resolution absorption gas phase spectra of electronic transitions of a series of carbon chain radicals as well as their D- and ^{13}C- substituted isotopologues. A systematic study of the spectra - recorded at low temperatures in the range of several kelvins - allows us to characterize the spectroscopic constants in ground an excited electronic states, and this also provides information on molecular structure. This thesis is structured as follows:

In chapter 3, optical absorption in the $\widetilde{A}^2\Delta - \widetilde{X}^2\Pi$ electronic origin band of the linear -hydro-carbon-chain radicals C_5H and C_5D has been reinvestigated. Cavity ring-down spectroscopy and two types of plasma nozzles, in a slit and a pinhole configuration, have been used. The data analysis yields a value for the spin-orbit splitting in the upper electronic $^2\Delta$ state of $l-C_5H$. A contour analysis of the unresolved band profiles makes it possible to an estimate for the $\widetilde{A}^2\Delta$ state lifetime of 1.6 ± 0.3 ps.

In chapter 4, it is shown that deuterium labeling of nonlinear hydrocarbon chains is a useful approach to characterize molecular structure. This method has been applied for two trihydrogenated carbon chain radicals, C_9H_3 and

$C_{11}H_3$, by recording optical transitions of both species and their (partially) deuterated equivalents in the 19000 cm^{-1} region using cavity ring-down spectroscopy and plasma expansions constituting C/H, C/D, and C/H/D nonlinear chains. The number of observed bands, the quantitative determination of isotopic shifts, and supporting calculations show that the observed C_9H_3 and $C_{11}H_3$ spectra originate from $HC_4(CH)C_4H$ and $HC_4[C(C_2H)]C_4H$ species with $C_{2\nu}$ symmetry.

Chapter 5 presents rotationally resolved $\widetilde{A}^3\Sigma_u^- - \widetilde{X}^3\Sigma_g^-$ gas phase absorption spectra of partially and fully deuterated linear HC_7D and DC_7D radicals. These carbon chain radicals are generated in a supersonically expanding planar plasma, discharging a diluted gas mixture of acetylene and D-enriched acetylene in helium and argon. The spectral analysis of the recorded spectra yields accurate ground and excited state rotational parameters as well as origin band positions of HC_7D and DC_7D.

In chapter 6, a study of the $\widetilde{A}^1\Pi_u - \widetilde{X}^1\Sigma_g^+$ $000 - 000$ electronic band of tricarbon molecule (C_3) and its ^{13}C-substituted isotopologues is presented. Rotationally resolved absorption spectra of this origin band for all six isotopologues using cavity ring-down spectroscopy in a supersonically expanding planar plasma are observed. The band of $^{12}C_3$ is re-investigated, focusing on an experimental clarification of the rotational line intensities, and an extended Hamiltonian is presented to study a perturbation analysis of the $\widetilde{A}^1\Pi_u$ 000 upper state. For the five partially and fully ^{13}C substituted C_3 isotopologues spectra are presented and analyzed, resulting in a set of molecular constants characterizing the $\widetilde{A}^1\Pi$ 000 upper electronic state and the ground state molecular constants for two of the ^{13}C di-substituted isotopic species.

In chapter 7, we present for the first time $^2\Pi - \widetilde{X}^2\Pi$ electronic origin band spectra of long chain hydro-carbon radicals and their ^{13}C-fully substituted isotopologues ($^{13}C_8H$, $^{13}C_8D$, $^{13}C_{10}H$ and $^{13}C_{10}D$), as well as spectra with better S/N ratio for $C_{2n}H/D$, (n= $4 - 6$) species. A systematic study of the band profiles for different rotational temperatures provides information on estimate excited state rotational constants and to derive values for the upper state lifetimes.